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Polymerization of acrylonitrile catalyzed by lanthanide-sodium alkoxide clusters $Ln_2(OCH_2CH_2NMe_2)_{12}(OH)_2Na_8$ [Ln=Yb (1), Nd (2) and Sm (3)]

CAOYang[1], LI JunMei[1], WANG YaoRong[1*], YAO YingMing[1] & SHEN Qi[1,2*]

[1] *Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China;*

[2] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

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Polymerization of acrylonitrile was carried out using, for the first time, the lanthanide-sodium alkoxide clusters $Ln_2(OCH_2CH_2NMe_2)_{12}(OH)_2Na_8$ [Ln=Yb (**1**), Nd (**2**) and Sm (**3**)] as single component catalysts. These heterobimetallic complexes exhibit high activity and give atactic polyacrylonitriles with high molecular weight. The polymerization temperature can be varied over the range −78 to 50°C. The solvent has a substantial effect on the polymerization activity. The order of activity for solvents is DMF>DME ≈ toluene ≈ THF>hexane.

acrylonitrile, lanthanide, sodium, clusters, polymerization

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Polyacrylonitrile (PAN) is an important polymer, in part because it is the precursor for valuable carbon fibers [1], mesoporous carbons [2,3] and other materials [4]. PAN can be prepared by radical polymerization or anionic polymerization, and numerous metal complexes of alkali [5–7], alkaline earth [8,9] and late transition metals [10–14] have been reported as initiators for anionic polymerization of acrylonitrile. Various lanthanide metal complexes have also been found to be single-component initiators for anionic polymerization of acrylonitrile, including $[(tert\text{-}BuCp)_2NdCH_3]_2$ [15], $(ArO)_2Sm$ [16], $Ind_2LnN(i\text{-}Pr)_2$ (Ln=Y, Yb) [17], SmI_2 [18], $[(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)Y(CH_2SiMe_3)(THF)]$ [19], $La(C_5Me_5)[(CH(SiMe_3)_2)]_2(THF)$ [20], $Ln(SAr)_3(py)_3$ (La=Sm, Yb) [21], $Ln(OAr)_3$ (Ln=La, Y) [22] and $LLn(NPh_2)_2$ (THF) (L=*N,N′*-bis(2,6-dimethylphenyl)-2,4-pentanediiminate) [Ln=Yb, Nd] [23]. However, only a few lanthanide metal complexes show the desired catalytic activity, and most of these complexes are sensitive to air and moisture. Consequently development of highly active lanthanide catalysts that are readily available and easy to handle is an important objective.

Multinuclear metal complexes offer the possibility of unique and more selective catalytic behavior by facilitating cooperation effects between active sites. Heterobimetallic complexes of lanthanide and other metals have been found to be versatile catalysts for polymerization of various nonpolar and polar monomers [24–28]. We have also reported that anionic lanthanide phenoxides are more active than the corresponding lanthanide triphenoxides without alkali metals, for the ring-opening polymerization of ε-caprolactone [29]. Very recently, we have found that the lanthanide-sodium alkoxide clusters $Ln_2(OCH_2CH_2NMe_2)_{12}(OH)_2Na_8$ (Ln=Nd, Sm, Y, Ho), which are not only easy to prepare but are also quite stable, are extremely active catalysts for the polymerization of ε-caprolactone and trimethylene carbonate [30]. However, no example of polymerization of AN using a

*Corresponding authors (email: yrwang@suda.edu.cn; qshen@suda.edu.cn)

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heterobimetallic lanthanide complex has been reported. In the course of our study on the reactivity of bimetallic complexes of lanthanide and alkali metals, we have examined the activity of lanthanide-sodium alkoxide clusters for the polymerization of acrylonitrile. Preliminary results revealed that $Ln_2(OCH_2CH_2NMe_2)_{12}(OH)_2Na_8$ [Ln=Yb (**1**), Nd (**2**), Sm (**3**)] showed high catalytic activity for the polymerization of acrylonitrile: the activity is higher than that of NaOR, indicating the existence of a cooperative effect of lanthanide and sodium. Polymerizations with these clusters give polymers with high molecular weight and small amounts of branched structures. In this communication we report the results of these experiments.

1 Experimental section

1.1 General procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture, using standard Schlenk techniques.

1.2 Materials

THF, toluene, hexane, *N, N*-dimethylformamide (DMF) and dimethoxyethane (DME) were purchased from Nanjing Chemical Reagent Co. Ltd. (Nanjing, China), degassed and distilled from sodium benzophenone ketyl under argon prior to use. Acrylonitrile was purchased from Alfa Aesar, dried with CaH_2 and then distilled under argon. The complexes $Ln_2(OCH_2CH_2NMe_2)_{12}(OH)_2Na_8$ (Ln=Yb, Nd, Sm) were synthesized according to reported methods [30].

1.3 Acrylonitrile polymerization

The procedures for the polymerization of acrylonitrile initiated by complexes **1**, **2** and **3** were similar, and a typical polymerization procedure is given below. A 50 mL Schlenk flask, equipped with a magnetic stirrer bar, was charged with a solution of acrylonitrile (0.69 mL, 10.49 mmol) at 22°C. To this solution the desired amount of $Yb_2(OCH_2CH_2NMe_2)_{12}(OH)_2Na_8$ (42.57 mg, 0.0263 mmol) in toluene (0.69 mL) was added by syringe. The color of the reaction mixture changed to intense orange-red as soon as the initiator solution was added. The contents of the flask were stirred vigorously at room temperature for the desired time. The reaction mixture was then quenched by addition of 5% HCl-ethanol solution, and poured into ethanol to precipitate the polymer, which was dried under vacuum and weighed.

1.4 Characterization

^{13}C NMR spectra of polymers were obtained in DMSO-d_6 with a Unity Inova-400 spectrometer. The triad tacticities (mm, mr, and rr) of PAN were determined from the ratio of intensities for 3 methine-carbon peaks (26.8 for mm, 27.4 for mr and 27.9 for rr) in the spectra [31]. The intrinsic viscosities of polymer solutions in DMF at 25°C were determined with an Ubbelohde-type viscometer, and the viscosity-average molecular weights (M_η) were calculated from the equation $[\eta]=2.43\times10^{-2} M_\eta^{0.75}$ [32].

2 Results and discussion

2.1 Polymerization features

The lanthanide-sodium alkoxide clusters $Ln_2(OCH_2CH_2NMe_2)_{12}(OH)_2Na_8$ [Ln=Yb (**1**), Nd (**2**), Sm (**3**)] were prepared in high yield by one-pot reaction of $LnCl_3$ with 6 equiv of $Na(OCH_2CH_2NMe_2)$ and 1 equiv of NaOH, followed by simple crystallization without cumbersome purification [30]. The catalytic activity of these lanthanide-sodium alkoxide clusters for the polymerization of acrylonitrile was evaluated and the preliminary results are shown in Table 1. It is apparent that all of the clusters can act as initiators and there was almost no difference in activity between them. For example, the conversion was 91% for cluster **1** at room temperature for 10 min with [M]/[I]=400 (mole ratio), and 95% for cluster **2** and 90% for cluster **3** under the same conditions. Similar results were reported for polymerization initiated by $Ln(SAr)_3(Py)_3$ [21]. However, the results are different from those for polymerization of ε-caprolactone using heterometallic clusters as initiators, for which the activity is highly dependent on the ionic radius of the metal [30]. For that reason the catalytic activity of $NaOCH_2CH_2NMe_2$ for acrylonitrile polymerization was investigated to assess whether lanthanide metals made a contribution to the high activity of the clusters. The sodium complex $NaOCH_2CH_2NMe_2$ initiated polymerization of acrylonitrile, but the activity was much lower than for the clusters (Table 1), indicating that the presence of lanthanide metals resulted in increased activity. The data in Table 1 also show that the clusters have extremely high activity. Taking the system

Table 1 Polymerization of acrylonitrile in the presence of various catalysts [a)]

Initiator	[M]/[I]	Conversion (%)	M_η ($\times10^{-4}$ g mol^{-1})
1	400	91	2.43
	700	84	3.09
	1000	77	3.90
	2000	52	4.14
2	400	95	2.03
	700	87	2.59
3	400	90	2.12
	700	85	2.83
$NaOCH_2CH_2NMe_2$	117	46	4.08

a) Polymerization conditions: solvent, toluene; solvent/monomer = 1/1 (v/v); polymerization temperature, 22°C; polymerization time, 10 min.

with cluster **1** as an example, even when the molar ratio [M]/[**1**] was increased to 1000, the conversion still reached 77% (Table 1). To our best knowledge, this is the most active known lanthanide catalyst [15–20,22,23]. All of the polymers obtained using the lanthanide-sodium alkoxide clusters had high molecular weight (M_η>10^4 g mol^{-1}).

The influence of temperature on the polymerization is shown by the data in Table 2. The conversion decreased with decreasing temperature, while the molecular weights of the resulting polymers increased. This might be attributable to lower initiation efficiency and slower side reactions at the lower temperatures. It is worth noting that polymerization of acrylonitrile was conducted in a broad range of temperatures from −78 to 50°C using these clusters as initiators. The conversion obtained at the lowest temperature was still 65% (Table 2), which is another remarkable feature of these initiators.

The solvent had a substantial effect on the polymerization of acrylonitrile (Table 3). The conversion using cluster **2** was essentially quantitative within 10 min in DMF at room temperature with [M]/[I]=700, but the yield was only 64% in hexane under the same conditions. The order of activity for solvents was DMF>DME ≈ toluene ≈ THF>hexane. This order might be related to the differences in the solubility of polyacrylonitrile in these solvents. The molecular weights of the polymers were also solvent dependent. The molecular weight of the polymer obtained in DMF was the lowest, which might be because of side reaction(s) occurring during polymerization.

To gain further insight into the polymerization of acrylonitrile in the presence of the clusters, the relationship between conversion and reaction time for polymerization initiated by cluster **1** under optimized conditions was determined. Figure 1 shows that the polymerization proceeded very rapidly at 22°C. Both conversion and molecular weight of the resulting polymers increased with increasing time, and reached a plateau after approximately 10 min.

Table 2 Effect of temperature on the polymerization of acrylonitrile [a)]

Temperature (°C)	Conversion (%)	M_η (×10^{-4} g mol^{-1})	Tacticity (%)		
			mm	mr	rr
−78	65	7.14	28.7	46.3	25.0
−20	67	5.47	30.9	43.8	25.3
0	75	5.93	31.9	43.1	24.9
22	84	3.09	32.9	43.0	24.0
50	88	2.59	28.4	47.7	23.9

a) Polymerization conditions: solvent, toluene; solvent/monomer=1/1 (v/v); initiator, cluster **1**; [M]/[I]=700; polymerization time, 10 min.

Table 3 Solvent effects on the polymerization of acrylonitrile [a)]

Solvent	Conversion (%)	M_η (×10^{-4} g mol^{-1})	Tacticity (%)		
			mm	mr	rr
Hexane	64	2.42	30.6	43.4	26.0
THF	86	1.01	32.7	39.2	28.1
DMF	100	0.16	35.5	27.7	36.9
DME	90	2.60	34.8	44.6	20.6
Toluene	87	2.13	30.9	42.1	26.9

a) Polymerization conditions: solvent/monomer=1/1 (v/v); initiator, cluster **2**; [M]/[I]=700; polymerization temperature, 22°C; polymerization time, 10 min.

2.2 Microstructure of PAN

Figure 2 shows the ^{13}C NMR spectrum of a representative PAN sample produced using cluster **1**. The tacticity of PAN was determined from the –CH_2C(CN)H– methine resonance at 27 [31], and the results in Tables 2 and 3 indicate that all of the polymers obtained were atactic. Similar results were found for polymerization of acrylonitrile initiated by Ln$(SAr)_3(py)_3$ (La=Sm, Yb) [21], Ln$(OAr)_3$ (Ln=La, Y) [22] and LLn$(NPh_2)_2$(THF) [23]. It can also be seen from Figure 2 that there is a small peak at about 14, in addition to the main-chain –CH_2C(CN)H– resonances. The peak at 14 is assigned to the carbon atoms in branched PAN, as suggested by Kamide and co-workers [33]. To address the influence of polymerization temperature on the microstructure of the polymers, we obtained ^{13}C NMR spectra of the polymers that were synthesized in toluene at 50 and −78°C. Figure 2 shows that the intensity of the peak at 14 for the polymer formed at 50°C was stronger than for the polymer produced at −78°C. This trend is reasonable because the branching reaction can be efficiently suppressed at low temperature. In addition, the solvent had an apparent effect on the microstructure of the PANs that were obtained. With DMF as solvent, a strong peak at about 14 was observed in the ^{13}C NMR spectrum, indicating a substantial amount of branched polymer. By contrast, PANs with small amounts of branched structure were prepared using hexane or THF or DME as the solvent. Similar results were observed with

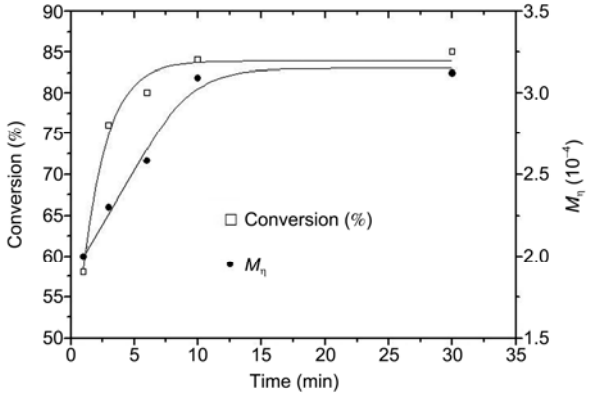

Figure 1 Relationship between reaction time, conversion and molecular weight. Polymerization conditions: solvent, toluene; solvent/monomer = 1/1 (v/v); initiator, cluster **1**; [M]/[I]=700; polymerization temperature, 22°C.

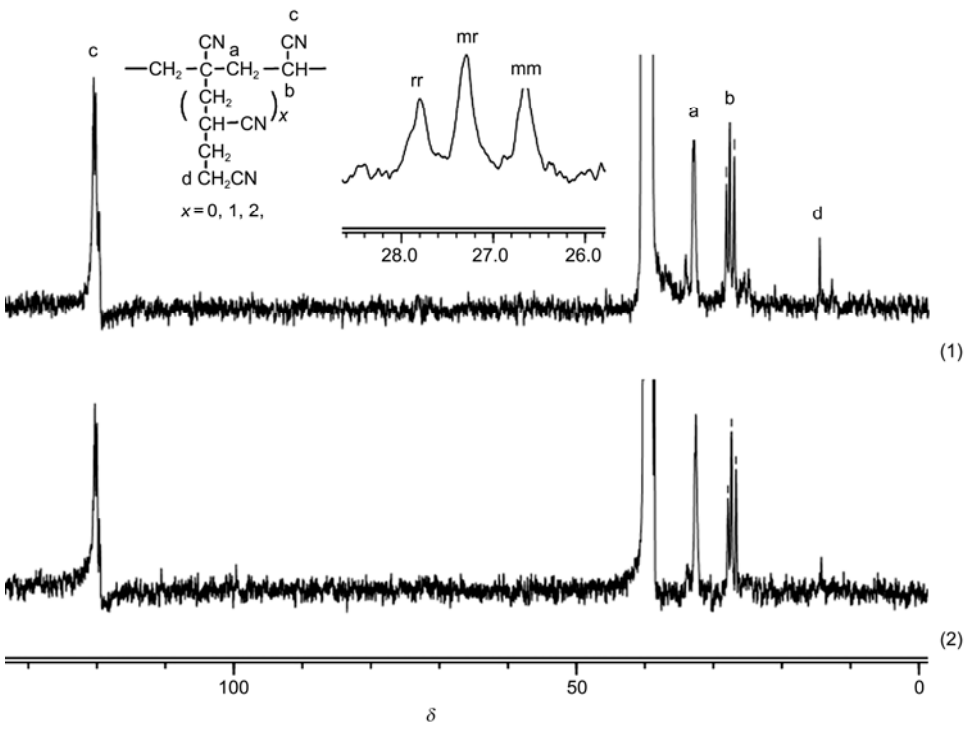

Figure 2 ^{13}C NMR spectra of PAN synthesized in toluene, using cluster **1** as initiator. (1) 50°C; (2) −78°C.

$Ln(OAr)_3$ (Ln=La, Y) as catalysts [22]. All of these results indicate that polymerization of acrylonitrile with the new clusters proceeds by an anionic mechanism.

3 Conclusions

The lanthanide-sodium alkoxide clusters $Ln_2(OCH_2CH_2NMe_2)_{12}(OH)_2Na_8$ [Ln=Yb (**1**), Nd (**2**) and Sm (**3**)] were found to be efficient catalysts for polymerization of acrylonitrile, giving atactic polyacrylonitrile with high molecular weight. The polymerization can be carried out over a broad range of temperatures from −78 to 50°C, and the amount of branched polymer formed can be reduced by decreasing the polymerization temperature.

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